



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
75 Hawthorne Street
San Francisco, CA 94105-3901

June 23, 1999

MEMORANDUM

SUBJECT: Regional Interim Policy for Determination of Volatile Organic Compound (VOC) Concentrations in Soil and Solid Matrices.

FROM: Nora McGee, Assistant Regional Administrator
USEPA Region 9

TO: USEPA Region 9 Personnel and Parties Collecting Environmental Measurements Under Regional Programs.

Purpose

Appropriate methodologies to minimize volatilization and biodegradation losses in solid matrices have not been consistently implemented throughout Region 9. This memorandum articulates the Region's policy on the adoption of sampling and laboratory methodologies for the collection of volatile organic compound (VOC) data from soil or solid matrices. USEPA SW-846, Update III, Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," incorporating procedures to minimize VOC losses was finalized by USEPA in June 1997. This Region 9 policy requires the use of Method 5035, or an equally or more effective method, for the collection of representative and precise data for VOCs in soil and solid matrices. Additionally, this policy was developed to be consistent with the Agency's Data Quality Objectives (DQO) Process (outlined in "Guidance for the Data Quality Objectives Process," USEPA QA/G-4, September 1994) by allowing for a graded approach through the collection of representative data that meets project data quality needs.

Policy

Scope and Applicability

Environmental data collection activities performed under USEPA Region 9 programs for the determination of VOC concentrations in soil and solid matrices.

This policy is applicable to data collection activities conducted by USEPA staff and contractors, USEPA grantees, Federal Facilities, entities complying with USEPA regulatory requirements and/or other entities producing data for USEPA decision making. This includes data being collected under ongoing quality assurance plans and sampling plans.

INTERIM POLICY

Time Frame for Implementation

This policy should be adopted quickly and to the maximum practicable extent. Cases where it is not practicable to implement this policy should be brought to the attention of the USEPA Region 9 QA Office. This is being put forth as an interim policy, as USEPA is still evaluating technical information to further refine procedures for minimization of VOC losses. Please note, an amendment to this policy may be required.

Statement of Policy

Methods for the collection and analysis of VOCs in soil or other solid matrices must minimize volatile losses. Because USEPA SW-846 Method 5035 does not rigorously dictate specifics of field sample collection¹ and laboratory sample handling protocols, project specific procedures to minimize volatile losses must be developed and be included in the site/program quality assurance project plan (QAPP) or sampling and analysis plan (SAP). USEPA SW-846 Method 5021 “Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis,” also incorporates procedures to minimize volatile losses. However, Method 5021 should be used with caution, as it can be reasonably interpreted and performed in a way which does not prevent loss of VOCs. USEPA Region 9 considers the following practices as minimum requirements to reduce volatile losses in soil samples:

1. Samples are handled as intact² soil cores in the field and laboratory.
2. Samples are stored in containers which can be reliably sealed to prevent volatilization losses³ over the project specified analytical holding time.
3. Samples are analyzed or chemically, acid or methanol, preserved within 48 hours of collection, if any contaminant may undergo biodegradation.
4. Exposure of the sample core to the atmosphere in the field and laboratory should be minimized⁴.

¹ ASTM Method D4547-98 “Standard Guide for Sampling Waste and Soils for VOCs,” is a good reference for VOC sampling protocols.

² Soils should always be collected and transferred using a coring device, such as a metal sleeve or cut off syringe. Use of transfer devices, such as spatulas, is not acceptable either in the field or laboratory.

³ Volatilization losses from sampling/storage containers must be less than what would be expected from a volatile organic analysis vial with a Teflon/silicon septa stored for 14 days, unless project DQOs require more stringent requirements.

⁴ Field sub-cores should be taken immediately upon exposing the soil core to ambient conditions. Sub samples should be directly extruded into the analysis containers. Total exposure of samples to ambient conditions should not be more than 15 seconds.

INTERIM POLICY

USEPA Region 9 will consider exceptions to this policy on a case-by-case basis. All deviations from procedures outlined in Method 5035 should be documented in a QAPP or a SAP which must be submitted to, and approved by, the Region 9 QA Office. Additionally, the party responsible for data collection must demonstrate that the methodologies proposed will result in data that meet project/program data quality objectives (DQOs).

Additional Considerations

Field Laboratories: The use of field laboratories, that analyze samples within several hours of collection, is an excellent choice to prevent loss of volatiles in transit and storage. However, the sample collection and analysis procedures used must prevent volatilization losses and comply with requirements 1 and 4 articulated in the Statement of Policy. Additionally, the quality control criteria and quality assurance system used by a field laboratory must be adequate for generation of data which will meet project DQOs.

Addition of Surrogates and Matrix Spiking Compounds in the Field: The most appropriate time for addition of analytical surrogate and matrix spiking compounds into soils is prior to sample extraction, by water or a solvent. Method 5035 does not incorporate the addition of the compounds prior to extraction in the field. Because this is an important control check on the analytical process, which begins at extraction, for some project/program DQOs it may be appropriate to incorporate a procedure which adds surrogate and/or matrix spiking compounds prior to extraction.

Holding Times: The holding time for preserved soil samples should be interpreted as 14 days from the time of sample collection (stored at $4 \pm 2^\circ\text{C}$). Due to potential biodegradation losses, samples stored in sealed containers, but not chemically preserved, should not be stored for more than 48 hours. On a project/program specific basis, USEPA Region 9 will consider other alternatives to extend the holding time of soils that have not been chemically preserved (see Attachment A). Holding time will be considered as cumulative (see Attachment B for holding time examples). Exceptions should be documented in a QAPP or a SAP submitted to and approved by the Region 9 QA Office.

Unconsolidated Solid Matrices: Solid Matrices that are not amenable to the use of a coring technique should be collected in such a way as to preserve the integrity of the sample matrix. Transferring of these soils with spatulas or similar devices into sampling containers is discouraged as this disrupts the sample pore spaces and greatly increases the sample surface area available for volatilization. For soil piles, fresh soil at an adequate depth should be sampled.

Calcareous Soils: Method 5035 notes that, “Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial.” Calcareous soils that effervesce on contact with the low-level preservative solution should be collected using an alternative preservation technique (see Attachment A).

Soil Gas: This policy is not intended to address the role of soil gas in the environmental decision making process. The Region recognizes that soil gas data is used extensively, in USEPA Region 9, for site decision making and in some cases soil gas is the preferred tool for gathering data on subsurface conditions. However, there are also scenarios where soil gas data are unacceptable for agency decision making (e.g., in excavated soils and when determining disposal options).

Drilling Techniques: This policy does not address the impact of drilling techniques on the collection of a representative VOC sample. Site/program QAPPs and SAPs should address the impact of all collection techniques on sample integrity and select those appropriate for the DQOs. Potential VOC losses due to drilling techniques include, but are not limited to: sample compression and loss of pore space; air introduction into the sample matrix; heat introduced in the drilling process; and volatilization from prolonged periods in a non-hermetically sealed sampling apparatus.

Background

Traditional practices for the sampling and analysis of volatile organic compounds (VOCs) in soil have been shown to have a significantly low bias of inconsistent magnitude (Grant, 1996) from volatilization (Hewitt, 1996) and biodegradation (Hewitt, 1994). Based on this and other research, the USEPA modified the methodology in SW846 for collection and analysis of volatiles in soil. Soil was deleted as an option from Method 5030 and Method 5035 and Method 5021 were added. These methods provide for handling of samples as intact soil cores, chemical preservation techniques, storage of samples in hermetically sealed containers and minimization of analyte losses due to direct volatilization (both in the field and the laboratory) and biodegradation.

“Traditional” collection techniques, such as transferring soils to a glass jar with minimal head space and collecting samples directly into a brass sleeve (e.g., CA Split Spoon) do not yield accurate or consistent results. It has been specifically demonstrated that capped brass sleeves show significant losses. Hewitt and Lukash (Hewitt, 1996) demonstrated capped sleeves can show substantial losses in less than one day. Hewitt and Lukash also demonstrated volatile losses in uncapped core liners of up to 90% in less than 40 minutes for trichloroethene (TCE). Because other analytes and matrix types can have higher mobility than those tested, substantial losses may occur in an even shorter period of time. Grant, Jenkins and Mudambi (Grant, 1996) examined split sampling results from a cross section of laboratories. For VOCs in soil they noted that, “The magnitude of this scatter [for a typical data comparison] is so large that it is

impossible to recommend effective limits of acceptability. Instead, we believe that steps are urgently needed to improve data quality.” Hewitt noted (Hewitt, 1994) that biodegradation of Benzene and Toluene in soil samples stored in sealed glass ampules at 4 C for 14 days could be substantial, demonstrating a need for chemical preservatives. Turriff and Reitmeyer (Turriff, 1998) demonstrated that a variety of soil matrices could be held for 48 hours at 4 C, in sealed zero headspace containers, without substantial VOC losses. Additionally, Turriff and Reitmeyer demonstrated that freezing was an option to extend holding times of En Core™ sampling devices. Because volatile losses have been linked to disturbance of the soil matrix and exposure to the atmosphere, samples should be handled in intact soil cores and stored in hermetically sealed vessels in both the field and the laboratory.

This USEPA Region 9 policy is based on the best scientific information available at this time and is subject to further clarifications and additions as other research becomes available. If you have any questions please call Vance Fong at 415 744-1492 or Mathew Plate at 415 744-1493.

References

Hewitt, A.D. (1994) Concentration Stability of Four Volatile Organic Compounds in Soil Subsamples. US Army Cold Regions Research and Engineering Laboratory, Special Report 94-6.

Grant, C.L., T.F. Jenkins and A.R. Mudambi (1996) Comparison Criteria for Environmental Chemical Analyses of Split Samples Sent to Different Laboratories, Corps of Engineers Archived Data. US Army Cold Regions Research and Engineering Laboratory, Special Report 96-9.

Hewitt, A.D. and J.E. Lukash (1996) Obtaining and Transferring Soils for In-Vial Analysis of Volatile Organic Compounds. US Army Cold Regions Research and Engineering Laboratory, Special Report 96-5.

Turriff, D. Ph.D. and C. Reitmeyer (1998) Validation of Holding Times for the EnCore™ Sampler. En Novative Technologies, Inc.

Attachment A

Preservation Alternatives: The following are preservation alternatives that may be appropriate for some projects/programs and are subject to project/program specific approval by the USEPA Region 9 QA Office.

Freezing of unpreserved samples: It has been shown in several studies that freezing of unpreserved soils is an effective means of slowing the biodegradation process. At this time, USEPA Region 9 will accept freezing of unpreserved soils as a method to extend holding times up to seven days on a project specific basis. While there is some evidence that freezing for longer periods may also be acceptable for some data needs, USEPA Region 9 does not believe that the current scientific evidence supports a longer holding time for frozen samples in most cases. Samples should be frozen in containers that have an air tight seal and can maintain this seal while frozen. Because water expands in the freezing process, VOA vials with water or samples with extremely high moisture contents may rupture the storage container.

Preservatives: Acids other than sodium bisulfate may be used to preserve low level samples. The choice of an alternative acid should be made in consultation with the USEPA Region 9 QA Office. In all cases the preserved sample pH should be ≥ 2 .

Sampling Containers: Currently the Region recognizes three sample collection/storage alternatives which can be used (other than acid/water or methanol, as specified in Method 5035).

1. A VOA vial with 5 mL of water without preservative and approximately 5 g of sample. Which must be analyzed within 48 hours of collection by closed system purge and trap.
2. A VOA vial with approximately 5 g of sample. Water must be introduced through the septa at time of analysis by closed system purge and trap. Sample must be analyzed within 48 hours of collection if stored at $4 \pm 2^\circ\text{C}$ or 7 days if frozen. (This alternative must be approved on a project specific basis.)
3. An En Core™ sampler which is analyzed or preserved within 48 hours of collection if stored at $4 \pm 2^\circ\text{C}$ or analyzed within 7 days if frozen. (Freezing of En Core™ samplers must be approved on a project specific basis.)

If requested, USEPA Region 9 QA Office will consider the applicability of other sampling containers/devices that have been demonstrated, with appropriate supporting documentation, to be adequate for collection and storage of VOCs.

INTERIM POLICY

Attachment B Examples of Holding Time Policy

- Example 1 Sample is placed into a vial without chemical preservative in the field (due to effervescence) and stored at $4\pm 2^{\circ}\text{C}$.
- Sample must be analyzed within 48 hours of collection.
- Example 2 Sample is collected into a hermetically sealed sub-coring and storage device in the field, stored at $4\pm 2^{\circ}\text{C}$ and transferred into a vial without chemical preservative in the laboratory.
- Sample must be analyzed within 48 hours of collection.
- Example 3 Sample is collected into a hermetically sealed sub-coring and storage device, transported/stored at $4\pm 2^{\circ}\text{C}$, frozen at the laboratory 28 hours after collection, defrosted after 2 days and transferred into a vial without chemical preservative in the laboratory.
- Sample must be analyzed within 20 hours from the time the sample is defrosted to $4\pm 2^{\circ}\text{C}$.
- $48 \text{ (hours allowed)} - 28 \text{ (hours before freezing)} = 20 \text{ (hours allowed from defrosting to analysis)}$